REACTIVE INTERMEDIATES
IN THE SYNTHESIS AND CHEMISTRY OF ORGANOSILACYCLES

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Abstract - The role of several organosilicon reactive inter-
mediates in the synthesis and chemistry of organosilacycles
will be illustrated with a variety of examples from our
laboratory. Particular emphasis will be placed on silanones,
siloxy radicals, and silenes. The discussion will be limited
to four, five, and six-membered rings.

INTRODUCTION

It is interesting to note that although silicon is directly beneath carbon
in the periodic chart, many of the systems which are called reactive inter-
mediates in organosilicon chemistry have quite stable analogs in carbon
chemistry. For example, silenes ($R_2Si=CR_2$), disilenes ($R_2Si=SiR_2$), and
silanones ($R_2Si=O$) have countless stable counterparts in the olefins and
carbonyl compounds of organic chemistry, but are known only as fleeting
intermediates. Indeed, it is only in the last decade that evidence has
been accumulating which appears to demand the existance of (p-p)π bonded
silicon (Ref. 1). As an example of two of these intermediates, some years
ago we established that the gas-phase flow pyrolysis of 1 resulted in aromat-
ization through extrusion of the bridge as dimethylsilene (2). When 1 was
copyrolyzed with benzaldehyde, there were obtained three major products --
styrene, hexamethylcyclotrisiloxane (D_3), and octamethylcyclotetrasiloxane
(D_4) (Ref. 2). The generally accepted mechanism for this process is cyclo-
addition of the silene to the carbonyl group to form silaoxetane, 3, which
decomposes to a molecule each of olefin and dimethylsilanone (4). Thus,
the cyclosiloxanes, D_3 and D_4, are believed to be the result of cyclic
oligomerization of 4. Indeed, insertion into an Si-O bond, as in the con-
version of D_3 to D_4, appears from all studies to date to be the best trap-
ping reaction of a silanone.
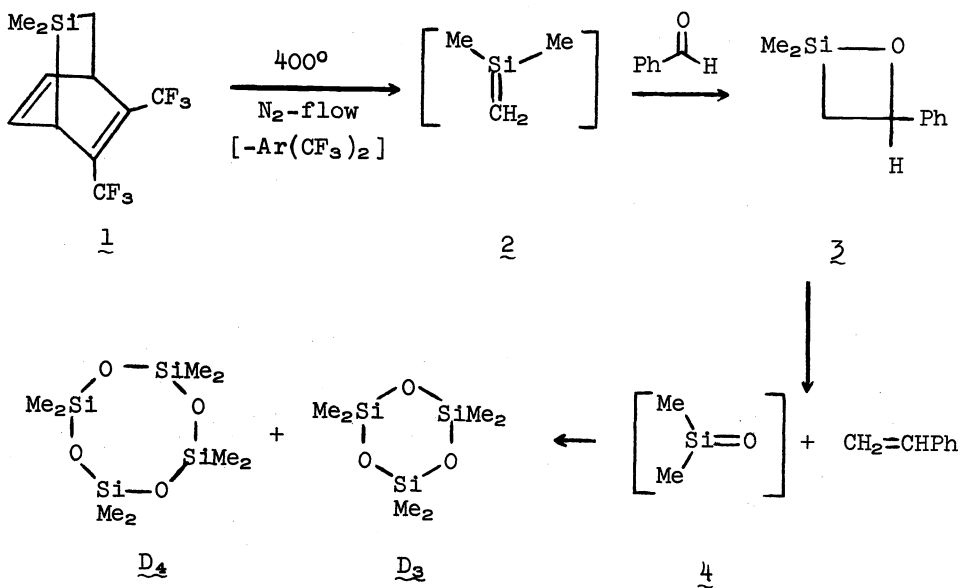
RESULTS AND DISCUSSION

A surprising feature of the silene-carbonyl reaction is that, although it has been examined by several groups, no one has ever observed a compound containing the silaoxetane ring system. Thus, in order to test this mechanism, and with the major goal of finding a milder and less complex route to silanones, we recently set out to synthesize this ring. An attractive possibility was the insertion of dimethylsilylene (5) into a C-O bond of the epoxide. In order to maximize chances of isolating the silaoxetane, the two mildest known methods for dimethylsilylene generation were employed - namely the thermolysis of hexamethylsilarane (6) (Ref. 3), and photolysis of dodecamethylcyclohexasilane (7) (Ref. 4).
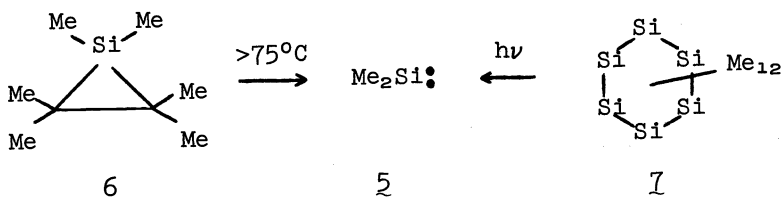
Heating a benzene solution of 6 and cyclooctene oxide (8) overnight produced a 73% yield of the deoxygenated product, cyclooctene. Although none of the silaoxetane 9 was observed, the product is consistant with the intermediacy of 9, and its decomposition through silanone extrusion. Further evidence for silanone intermediacy was obtained by performing the thermolysis in the presence of D_3, and obtaining D_4 in 54% yield.
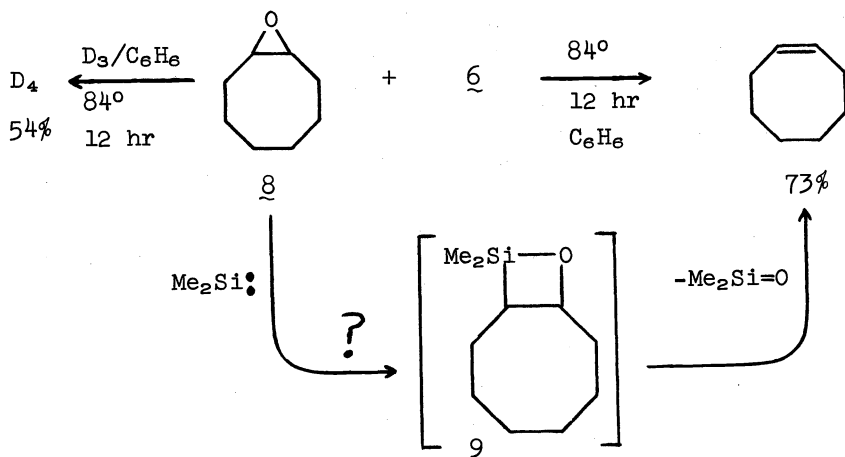
Turning to a reaction of even lower thermal requirements, the irradiation of a cyclohexane solution of silylene generator 7 and 8 affords a 76% yield of cyclooctene. Repeating the photolysis in the presence of D_3 again produces a high yield of D_4.
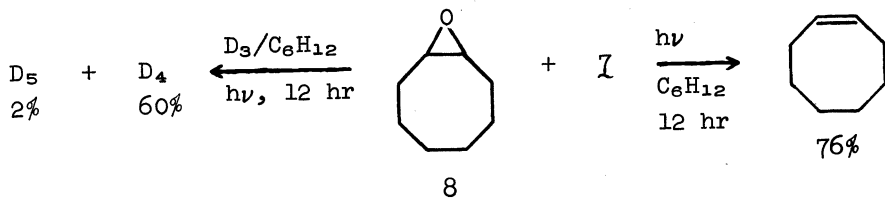
Obviously all of these results are consistent with silylene insertion into the C-O bond of the epoxide, and silanone extrusion from the resulting silaoxetane even at these relatively mild temperatures (Path A). However, the results are equally consistent with formation of an intermediate complex, such as a zwitterion, which either decomposes to silanone and olefin (Path B), or simply acts as a silanone transfer agent. Regardless of the mechanism, the silylene - epoxide reactions hold considerable promise for the synthetic use of silanones.

Path A — Me$_2$Si: + (epoxide/norbornene oxide) — Path B

Me$_2$Si—O (four-membered ring fused) → Me$_2$Si=O + (cyclohexene/norbornene) ← Me$_2$Si(Me)(Me)—O+ (epoxide)

Me$_2$Si=O + (alkene)

↓

Trapping
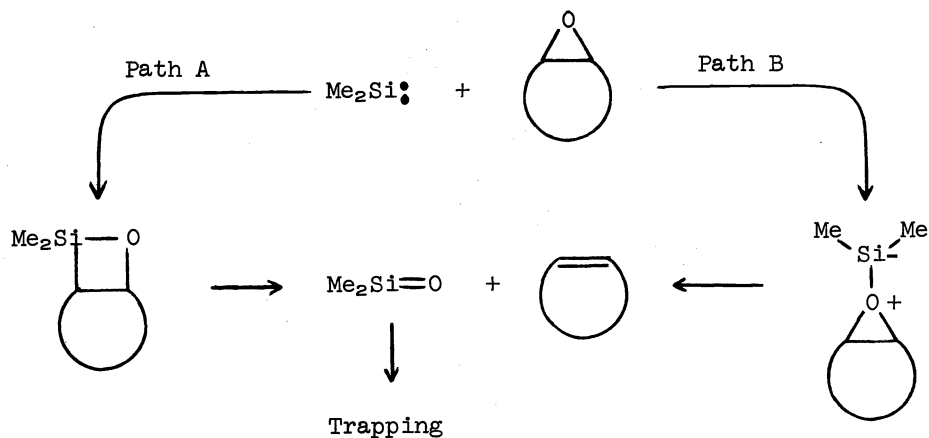
An example of the ring-closure routes to silaoxetanes which we have investigated is the reaction of dichloride 10 and activated magnesium. This room temperature reaction cleanly affords styrene (89%) and cyclosiloxanes D$_3$, D$_4$, and D$_5$. Again the results present a mechanistic dichotomy, as they are equally consistent with dechlorination to silaoxetane, or a direct fragmentation to styrene and dimethylsilanone.

O—CH$_2$
Me$_2$Si   CHPh $\xrightarrow[\text{25°, THF}]{\text{Mg}^*}$ (D$_3$ + D$_4$ + D$_5$) + PhCH=CH$_2$
 | |
 Cl   Cl   52%   89%

10   ↓?   →?

[O—
Me$_2$Si   →   O
        Ph   ‖
                   Si   +   (alkene)
                 Me   Me   Ph]
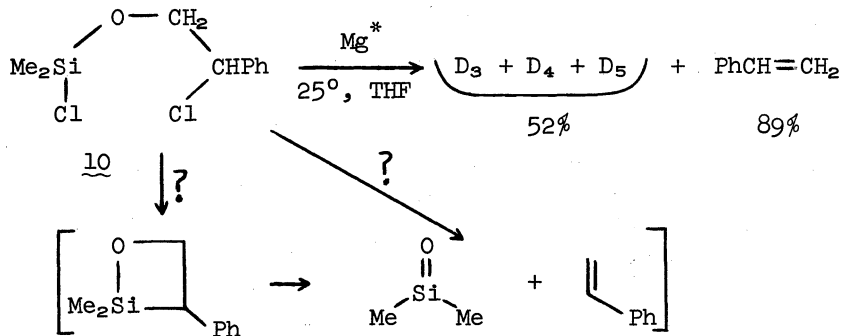
Another attempt to form a silaoxetane through cyclization employed as precedent the fact that silyl hydrides are cleanly etherified through Rh(I) catalyzed reaction with alcohols. Thus, we synthesized β-silylethanol 11 and heated it with (Ph$_3$P)$_3$RhCl in hopes of performing an intramolecular etherification to form the silaoxetane ring. Instead we obtained a small, but intriguing yield of D$_3$ and a 57% yield of the totally unexpected six-membered cyclic disiloxane 12.

CH$_2$—CH$_2$
Me$_2$Si   OH $\xrightarrow[\text{C}_6\text{H}_6]{(\text{Ph}_3\text{P})_3\text{RhCl}}$ D$_3$ + (ring 12)
        H   25°

11   6%   12   (57%)

This same ring, 12, was formed in 32% yield when we attempted to convert 11 into the silyl bromide and allow intramolecular cyclization to take place.

11 $\xrightarrow[\text{C}_5\text{H}_5\text{N}]{\text{Br}_2}$ D$_3$ + D$_4$ + 12 + (eight-membered ring)
        −78°   1%   1%   32%

46%

What we believe is happening in both reactions of 11 is that closure to silaoxetane does occur, and it is followed by extrusion of dimethylsilanone which can oligomerize to D_3 and D_4, but prefers to insert into the Si-O bond of the silaoxetane to afford 12.

Currently we are investigating an entirely different route to silanones, which is based on the precedent that alkoxy radicals are known to extrude alkyl radicals to form ketones. We wondered whether conditions and systems could be found where this analogous process would occur to convert siloxy radicals to silanones.

$$R_3C-O^{\cdot} \xrightarrow[-R^{\cdot}]{} R_2C=O$$

$$R_3Si-O^{\cdot} \xrightarrow[-R^{\cdot}]{?} R_2Si=O$$

Although bis(silyl)peroxides thermally rearrange, Davies (Ref. 7) has shown through ESR experiments that photolysis does produce siloxy radicals. Thus, it was decided to explore the fate of these radicals when no traps were present. Irradiation of bis(trimethylsilyl)peroxide in perfluorohexane is both rap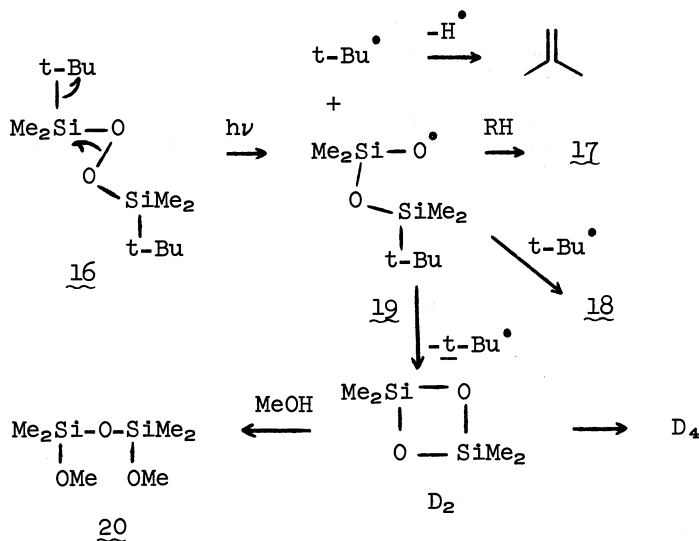id and clean, as it produces only three products, siloxanes 13, 14, and 15. Although the formation of the minor two products, 14 and 15, is consistent with insertion of dimethylsilanone units into the disiloxane 13 and the trisiloxane (14), when the photolysis is repeated with D_4 as the solvent there is no trapping of silanone to form D_5. Thus, we conclude that dimethylsilanone is not involved in this reaction. This conclusion essentially demands that the products are formed through S_H2 processes, with trimethylsiloxy radicals attacking starting material to displace the peroxy radical, and attacking 13 and 14 to displace methyl radicals and form 14 and 15 respectively.

As loss of a t-butyl radical will be easier than loss of a methyl radical, we synthesized peroxide 16 and subjected it to UV irradiation in perfluorohexane solution. The products were disiloxanes 17 and 18, isobutylene, and D_4. While it might be tempting to ascribe the formation of isobutylene and D_4 to generation of the siloxyl radical followed by decomposition to t-butyl radical and dimethylsilanone, it would be difficult to explain why the silanone oligomerized solely to D_4, and not to the usual mixture of D_3 and D_4. Indeed, photolysis of 16 in D_4 solvent afforded only a 2% yield of D_5.

D$_5$ (2%)

D$_4$ ↑ hν

$$\begin{array}{ccc} \text{Me} & & \text{Me} \\ | & & | \\ \text{t-Bu-Si-O-O-Si-t-Bu} \\ | & & | \\ \text{Me} & & \text{Me} \end{array} \quad \xrightarrow[\text{C}_6\text{F}_{14}]{\text{h}\nu}$$

16

$$\begin{array}{ccc} \text{Me} & & \text{Me} \\ | & & | \\ \text{t-BuSi-O-Si-OH} \\ | & & | \\ \text{Me} & & \text{Me} \end{array} \quad + \quad \begin{array}{ccc} \text{Me} & & \text{Me} \\ | & & | \\ \text{t-BuSi-O-Si-OtBu} \\ | & & | \\ \text{Me} & & \text{Me} \end{array}$$

17   18

CH$_2$
‖
Me   Me   +   D$_4$

(28%)

$$\left[\begin{array}{c} \text{Me} \\ | \\ \text{t-BuSi-O}^{\bullet} \\ | \\ \text{Me} \end{array} \quad \xrightarrow{?} \quad \text{t-Bu}^{\bullet} \quad + \quad \text{Me}_2\text{Si=O} \right]$$

As we must therefore conclude that little (if any) silanone is being formed in the photolysis of 16, how are the products to be explained? It seems reasonable that all arise from a single intermediate, 19, which is formed when the excited peroxide decomposes through intramolecular displacement of a t-butyl radical. Disiloxyoxy radical 19 can either abstract a hydrogen to form 17, combine with t-butyl radical to form 18, or perform a second intramolecular displacement of t-butyl radical to afford the oft-postulated cyclodisiloxane, D$_2$. The dimerization of D$_2$ provides an explanation for the exclusive formation of D$_4$. More definitive evidence for the intermediacy of D$_2$ was obtained by conducting the photolysis of 16 in the presence of a six-fold excess of methanol to obtain the expected methanol addition product, 20, and a total disappearance of D$_4$.

t-Bu
|
Me$_2$Si—O
O
SiMe$_2$
|
t-Bu

16

hν →

t-Bu$^{\bullet}$ $\xrightarrow{-H^{\bullet}}$

+

Me$_2$Si—O$^{\bullet}$
|
O—SiMe$_2$
|
t-Bu

19

$\xrightarrow{\text{RH}}$ 17

t-Bu$^{\bullet}$ → 18

| $-$t-Bu$^{\bullet}$
↓

Me$_2$Si—O
| |
O—SiMe$_2$

D$_2$

→ D$_4$

Me$_2$Si-O-SiMe$_2$
| |
OMe   OMe

20

$\xleftarrow{\text{MeOH}}$

Since 1973, it has become established that the intramolecular reaction of α-silylcarbenes produces silenes (Ref. 6). However, the systems studied to date have been complicated by a variety of alternate reaction pathways. Thus, we chose to study the simple, symmetrical system, bis(trimethylsilyl)-carbene, 22, whose steric bulk precludes dimerization, and sheath of methyl groups presents the possibility for competition between C-H insertion and methyl migration.

Carbene 22 was generated both photochemically and thermally from bis(tri-methylsilyl)diazomethane (21). Both methods produce the same 1,3-disila-cyclobutane, 24, clearly arising from methyl migration to produce silene 23 which undergoes head-to-tail dimerization. The thermal reaction also
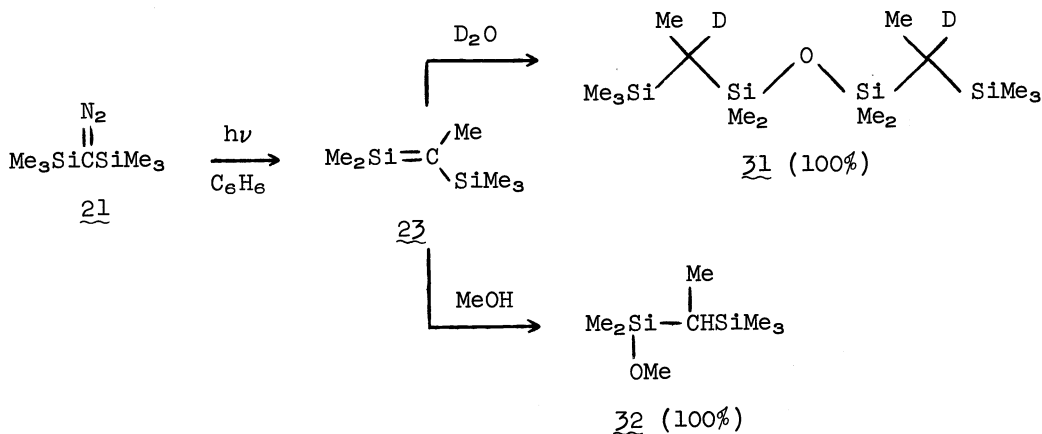
produces a linear dimer, 25, arising from head-to-head dimerization, followed by intramolecular hydrogen abstraction.
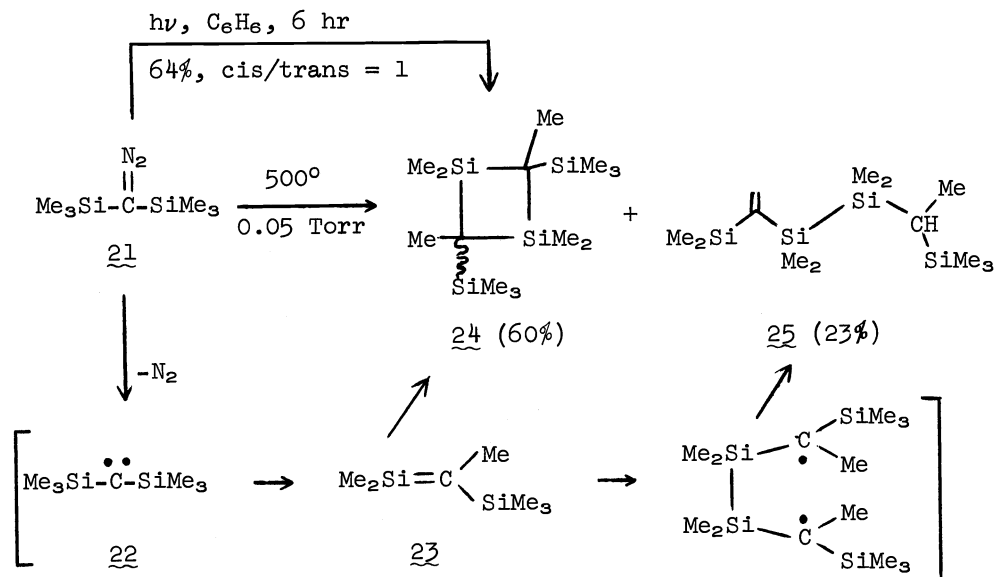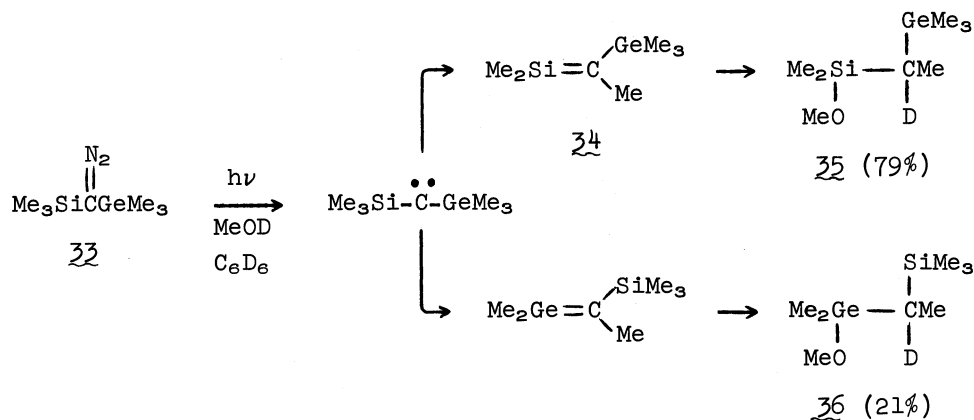

The flow copyrolysis of 21 and benzaldehyde illustrates how efficient is the generation of silene 23. Only three products are produced (26, 27, 28) in 97% combined yield and 98% mass balance. Each of these products clearly arises from the intermediacy of 23. Addition of silene 23 to the carbonyl group produces diradical 29, which can either close to silaoxetane 30 and extrude dimethylsilanone to yield olefins 26 and 27, or can intramolecularly abstract a hydrogen atom to form the benzylether, 28.
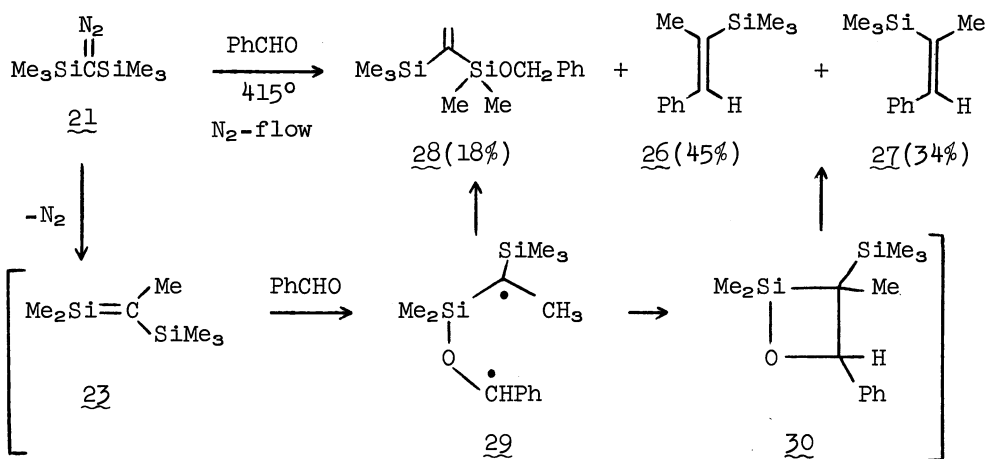
Efficiency of photochemical generation of silene 23 was dramatically demonstrated by irradiation of 21 in the presence of a three-fold excess of D_2O to quantitatively afford disiloxane 31. Likewise, quantitative formation of methoxysilane 32 was observed when methanol was substituted for D_2O.

$$Me_3SiCSiMe_3 \quad (N_2) \xrightarrow[C_6H_6]{h\nu} \quad Me_2Si=C\begin{smallmatrix}Me\\SiMe_3\end{smallmatrix}$$

21   **23**

$$\xrightarrow{D_2O}$$

Me_3Si–C(Me)(D)–Si(Me_2)–O–Si(Me_2)–C(Me)(D)–SiMe_3

31 (100%)

$$\xrightarrow{MeOH} \quad Me_2Si(OMe)-CH(Me)SiMe_3$$

32 (100%)

The mixed diazo compound **33** was constructed to set up a competition between silene and germene formation. Thermolysis in benzaldehyde produces products (76%) only from reaction of silene **34**. However, photochemical carbene generation produces both silene and germene as can be seen from the photolysis in the presence of MeOD. This reaction was extremely clean with only ethers **35** and **36** being formed in the combined yield of > 95%. Thus under these conditions silene production is favored over germene formation by a factor of four.

$$Me_3SiCGeMe_3 \quad (N_2) \xrightarrow[C_6D_6]{h\nu \quad MeOD} \quad Me_3Si-\ddot{C}-GeMe_3$$

33

$$\longrightarrow Me_2Si=C\begin{smallmatrix}GeMe_3\\Me\end{smallmatrix} \longrightarrow Me_2Si(OMe)-C(Me)(D)(GeMe_3)$$

34   **35** (79%)

$$\longrightarrow Me_2Ge=C\begin{smallmatrix}SiMe_3\\Me\end{smallmatrix} \longrightarrow Me_2Ge(OMe)-C(Me)(D)(SiMe_3)$$

36 (21%)

Germene generation was of course maximized from bis(trimethylgermyl)diazomethane (**37**). Pyrolysis of **37** produced **39** and **40**, each in ca. 32% yield. Dimer **39** clearly arises from head-to-head dimerization of germene **38**, while we believe that germazene **40** is a result of reaction between **37** and **38**. Thus, it would appear that **37** is a rather efficient thermal germene generator. Photochemical germene production is even more efficient, as irradiation of **37** produces dimer **39** in 89% yield, and irradiation in the presence of MeOD affords **41**, the product of methanol addition across the π-bond of germene **38**, in > 95% yield.

41 (>95%)

40 (32%)

37?

MeOD

38   hν ←   N₂ ‖ Me₃GeCGeMe₃   400° N₂-flow →   Me₂Ge=C⟨Me, GeMe₃

37

hν (89%)

39 (32%)

We have recently had considerable success in employing retroene elimination (Ref. 7) to the synthesis of unsaturated silacycles. For example, allylsila-cyclohexadiene 42 cleanly affords silatoluene (43) as evidenced by a variety of traps (Ref. 8). This elimination of propene from an unsaturated allyl-silacycle was also effectively used in the conversion of silacyclopentene 44 to methylsilole 46 (Ref. 9). In this thermolysis the initial product is the 1-silacyclopenta-1,3-diene, 45, which undergoes 1,5-hydrogen migration, followed by dimerization to 47. Although 46 was never observed, it can be quantitatively produced simply by heating of 47, as evidenced by the clean reaction with maleic anhydride to afford adduct 48.

430° HC≡CH (flow) −C₃H₆

42   43   (34)

820° vac.

1,5-H

44   45   46

48 (96%)   150°   47 (71%)

Most recently we have discovered a perhaps more exotic process in the thermolysis of allyldisilanes. Vacuum-flow pyrolysis of 1,2-diallyltetramethyldisilane (49) cleanly (and unexpectedly) produced 1,1,3,3-tetramethyl-1,3-disilacyclopentene (51) in 51% yield. A rationalization for this extraordinary behavior was that we were observing an unprecedented homoretroene elimination of propene, where one of the silicon atoms was bypassed to achieve the six-electron process. The resulting disilacyclopropane 50 could now undergo (the initially desired) homolysis of the strained Si-Si bond, cyclize, and ring expand to the five-membered ring.
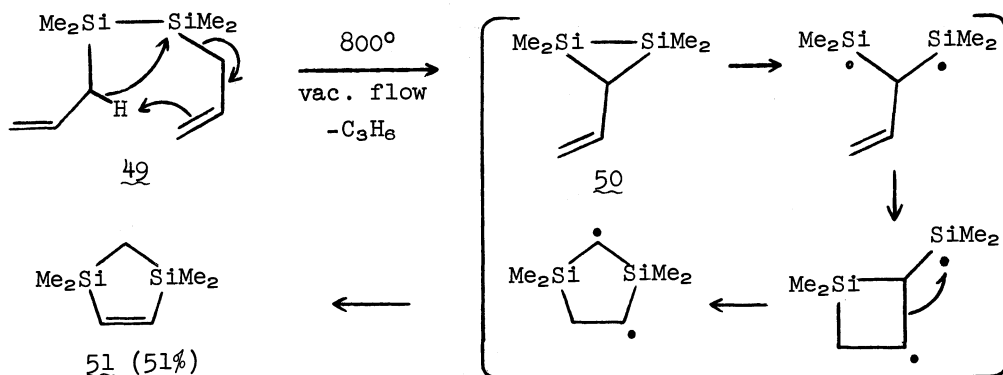
To put this mechanistic reasoning to a test, we replaced one of the allyl group of 49 with a benzyl group. Vacuum flow pyrolysis of 52 produced as the two major products, disilaindanes 54 and 55. Both of these products can be rationalized as originating from an initial homoretroene elimination of propene as illustrated here. The 1,2-disilaindane, 55, could also arise from allyl—Si homolysis followed by cyclization via intramolecular attack of silyl radical on the phenyl ring (labeling studies are in progress), but it is difficult to conceive of an alternate pathway to 54.
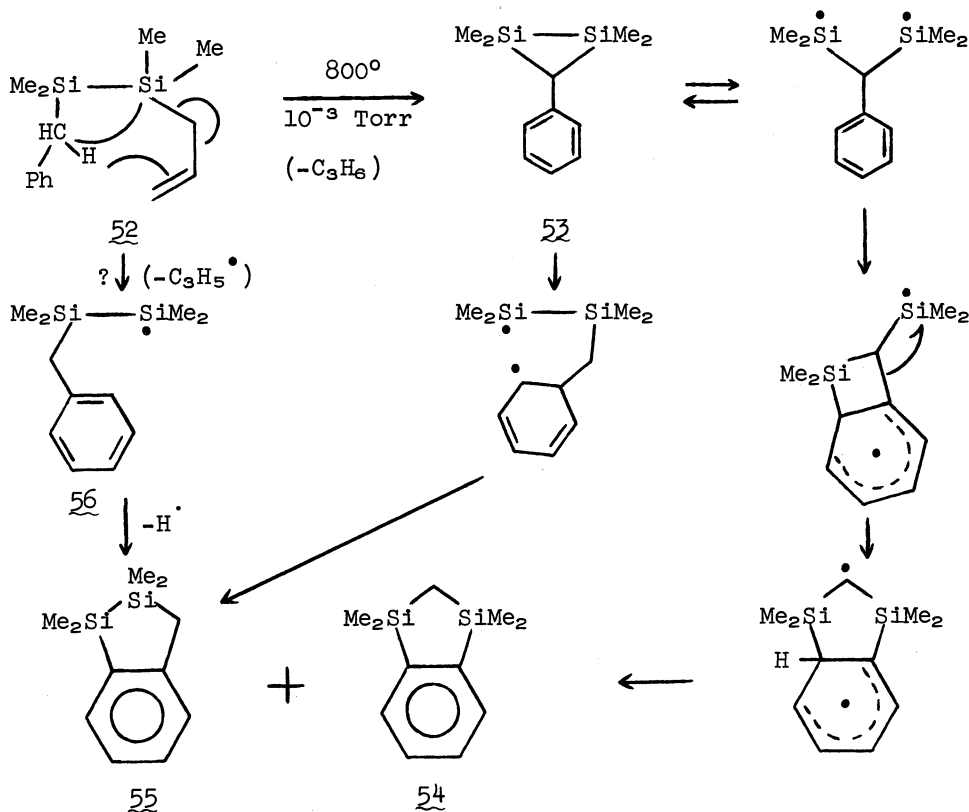
Apparently no special activation is required of the hydrogen being trans-
ferred in the homoretroene elimination, as thermolysis of allylpentamethyl-
disilane (57) produces as the major volatile product, 1,1,3-trimethyl-1,3-
disilacyclobutane (60). Again the formation of 60 is difficult to ration-
alize without the aid of the homoretroene mechanism. Elimination of propene
would afford tetramethylsilacyclopropane (58), which we would expect (Ref.
10) to undergo reductive elimination to form silylene 59. Silylene 59 has
been previously generated in our laboratory (Ref. 10), and it cleanly inserts
into a C-H bond to afford 60.
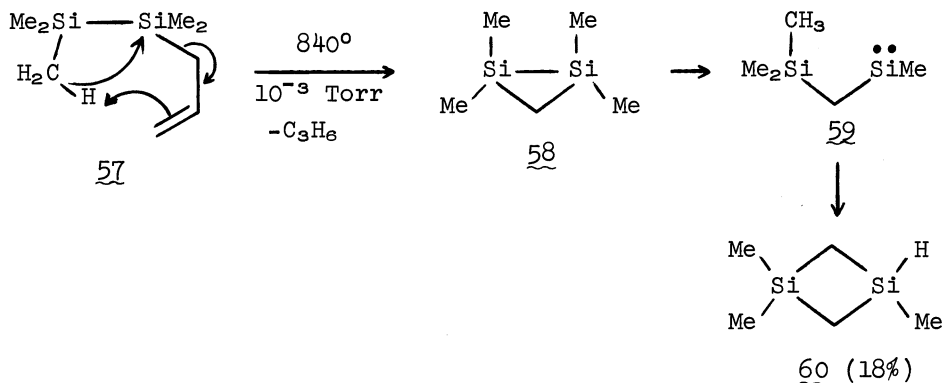
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